SCIENCE FOR CERAMIC PRODUCTION

SYNTHESIS OF ALUMINOMAGNESIAN SPINEL WITH EXCESS MAGNESIUM OXIDE UNDER VARYING FLOW RATES OF CATION MASS TRANSFER

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The synthesis of $MgAl_2O_4$ with 10 mol. % excess of MgO by heating a mixture of highly dispersed magnesium and aluminum oxide powders to 800 and 1100°C is investigated. The diffusion mass transfer rate of aluminum cations in the synthesis of spinel was accelerated by introducing a TiO_2 additive into Al_2O_3, whereas the mass transfer rate of magnesium cations was delayed by introducing a Na_2O additive into MgO. Simultaneously, spinel was synthesized without additives. The products of synthesis were investigated using petrography, x-ray phase analysis, and dissolution in HCl. The use of the additives and increasing the temperature of synthesis decrease the solubility of powders in HCl, which facilitates bringing initially formed solid solutions of Al_2O_3 in $MgAl_2O_4$ closer to the composition of stoichiometric spinel.

Aluminomagnesian spinel has a set of valuable physicochemical properties and finds application in the production of ceramics, primarily in the production of refractories. The $MgO – Al_2O_3$ system is sufficiently well studied, which makes spinel very convenient for using it as a model object.

The phase diagram shown in Fig. 1 indicates that as temperature increases, spinel, as a consequence of the formation of γ-nonstoichiometry [1], transforms into a typical variable-composition compound with a one-sided zone of existence; its composition is enriched only in aluminum oxide and can be represented by the formula $MgO \cdot Al_2O_3$. The author of [2] considers the effect of γ-nonstoichiometry on the inversion of spinel and interprets the formation of solid solutions of Al_2O_3 in $MgAl_2O_4$ in the context of classical thermodynamics.

The purpose of the present work is to study the synthesis of $MgAl_2O_4$ from a mixture of highly dispersed simple oxides with the content of MgO in excess of stoichiometric (10%; here and elsewhere mol.%, unless otherwise specified), using additives that are introduced in the initial simple oxides and change the rate of diffusion mass transfer in the synthesis of spinel.

Complex oxides (silicates, aluminates, chromites, ferrites, titanates, zirconates, etc.) are widely used in the technology of ceramics, glass, and binding materials. The diffusion rates of the cations forming a complex oxide, as a rule, are different, which produces a number of defects. If the diffusion rate of cations K_1 in a binary complex oxide is higher than that of cations K_2, then in the synthesis of the complex oxide from the initial simple oxides the reaction front becomes shifted toward the crystal of the oxide containing cation K_1 (the Kirkendall effect) [3] and pores emerge in the same crystal as well (the Frenkel effect) [4]. Furthermore, this leads to γ-nonstoichiometry in the complex oxide. Usually, at first we observe the formation of a solid solution of the oxide with the cation K_2 that has the lower diffusion rate in the complex oxide and a phase consisting of the oxide with the cation K_1 that has the higher diffusion rate, or a phase enriched in this oxide [5]. The existence of the second phase and the solid solution concentration affect all processes and properties of ceramics sensitive to them: sintering, electrophysical characteristics, high-temperature creep, etc.

A high degree of nonequilibrium of synthesis is ensured when the initial materials are mixtures of highly disperse powders of simple oxides. In such conditions, the oxide containing the faster cation K_1 proved to be in excess and can be identified and used to determine the cation that has the higher diffusion rate in the course of synthesis [6]. This is essential to know for the development of ceramic technology, in particular, for synthesis and sintering.

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It was assumed that the yield of stoichiometric spinel can be increased by modifying the mass transfer rates of aluminum and magnesium cations in synthesis. For this purpose, an attempt was made to bring the rate of aluminum cations mass transfer closer to the rate of magnesium cations or even make it higher by means of introducing additives in initial oxides and varying heat treatment regimes in the chemical reaction of spinel formation. In view of the above, this should create conditions for delaying the initial formation of a solid solution of Al_2O_3 in $MgAl_2O_4$ using initial highly disperse oxides. As a consequence, the composition of the resultant solid solution will approach the stoichiometric spinel composition sooner.

The modifying additives were selected as follows. A hypothesis was put forward in [5] that the formation of solid solutions of Al_2O_3 in spinel is the consequence of the fact that cations Al^{3+} diffuse more slowly than Mg^{2+} cations. Thus, by decreasing the diffusion rate of Mg^{2+} (by introducing an additive with sodium cations) and increasing the rate of diffusion of Al^{3+} (by introducing titanium additive) it can be expected that the rate of formation of a solid solution of Al_2O_3 in $MgAl_2O_4$ will be delayed. At the same time, the composition of the emerging spinel will approach the stoichiometric composition. Additives were introduced in an amount of 1% (above 100%). To develop a dominant concentration of respective vacancies, the homogeneity zone of the substitutional solid solution within 1% is quite sufficient. In this case the requirement imposed on the ratio between the radii of the host cations and the impurity cations is considerably less strict than for the formation of a wide homogeneity range, although it is desirable that the cations be close to each other in their radii and electronegativity.

The ionic radius of a sodium cation is larger than the radius of a magnesium cation, which increases the probability of its substitution for Mg^{2+} in magnesium oxide, instead of its penetration into an internode. The difference between the ionic radii of sodium and magnesium is 32%: 0.098 – 0.074 nm/0.074 nm, furthermore, both Na_2O and MgO have a cubic lattice. This facilitates the formation of a substitutional solid solution. The equation of the quasichemical reaction in this case can be written as follows:

$$Na_2O \xrightarrow{MgO} 2Na'_{Mg} + O_O + V_O^{\bullet\bullet}. \qquad (1)$$
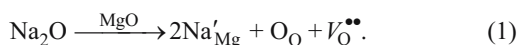
The difference between the sizes of the titanium and aluminum ions is 12%: 0.064 – 0.057 nm/0.057 nm. Titanium dioxide is commonly used to lower the production temperature of dense ceramics from α-Al_2O_3, which is related to the emergence of cation vacancies in the course of formation of the substitutional solid solution according to the following quasichemical reaction:
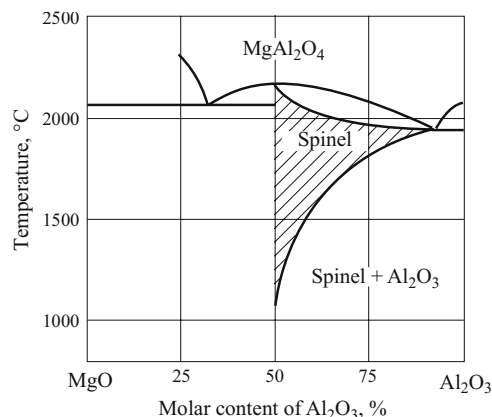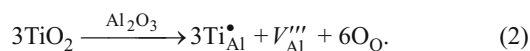
$$3TiO_2 \xrightarrow{Al_2O_3} 3Ti^{\bullet}_{Al} + V'''_{Al} + 6O_O. \qquad (2)$$

Fig. 1. Phase diagram of the $MgO – Al_2O_3$ system [1].

The initial materials were water-soluble salts of aluminum, magnesium, titanium, and sodium, as well as solid polyvinyl alcohol. To obtain highly dispersed powders of transition oxides and to achieve a uniform distribution of additives, we used a method which is a variation of the sol-gel method: distributing water-soluble salts in a matrix of polyvinyl alcohol gel [7].

Salt samples were weighed on an analytical scale to an accuracy of four decimal places taking into account calcination losses. The first corundum crucible was filled with $AlCl_3 \cdot 6H_2O$ and 1% (converted to Al_2O_3) salt $(HN_4)_2TiO(SO_4)_2 \cdot nH_2O$; the second crucible had $Mg(NO_3)_2 \cdot 6H_2O$ and 1% (converted to MgO) salt $NaNO_2$; after that distilled water and polyvinyl alcohol (its content in water 8 wt.%) were added up to complete the dissolution of the salts. Next, the gels were dried at 120°C for 36 – 48 h.

The dried gels were ground with a porcelain mortar to a size not larger than 1 mm and heat-treated up to the formation of a solid solution of the additive oxide and the main oxide. The gel with the aluminum salt was calcined at a temperature of 600°C for 1 h (heating and exposure lasted 4 h); the gel with the magnesium salt was heated at 800°C also for 1 h (heating and exposure lasted 6 h). According to x-ray phase analysis and petrography data, the highly dispersed powders obtained after calcination consisted only of magnesium and aluminum oxides.

Portions of these oxides were weighed on an analytic scale for the synthesis of spinel, with a 10% excess of magnesium oxide (60 mol.% MgO and 40 mol.% Al_2O_3, or 37.3 wt.% MgO and 62.7 wt.% Al_2O_3) compared to a stoichiometric composition.

The mixture of magnesium and aluminum oxides obtained after mixing in a planetary mill together with introduced additives was heat-treated for the synthesis of spinel at 800°C for 1 h (heating and exposure lasted 6 h) and at 1100°C with 2 h exposure.

The same operations on the same equipment and under the same conditions were simultaneously performed on powders without additives. They were also used to prepare mix-

TABLE 1

Presence of additives in mixture	Temperature of synthesis, °C	Weight loss, %
No additives	820	72.65
With additives	820	27.78
No additives	1120	20.22
With additives	1120	14.38

tures with 10% excess of MgO compared to a stoichiometric spinel composition.

After synthesis at 820 and 1100°C the powders (with and without additives) were divided into two parts. One part was treated with hydrochloric acid to remove free MgO. It was expected that MgO would dissolve in hydrochloric acid, whereas spinel and soinle-based solid solutions would not dissolve. A potion of the powder was dissolved in excessive hydrochloric acid (15.5 wt.%) at room temperature for 3 days under periodic stirring. The precipitate was rinsed with distilled water, filtered (blue ribbon filter), calcined, and weighed to determine the weight loss. The data on powder dissolution are given in Table 1.

After rinsing with distilled water on a filter, the powders were calcined at 600°C, then the filtrate was evaporated and calcined at 800°C to convert chlorides into oxides. Furthermore, the filtrate was additionally heat-treated at 1500°C for the phases to become well crystallized, which facilitated identifying the phase composition by x-ray phase analysis. The acid-treated powders, as well as the filtrate after rinsing, drying, and calcining the precipitate, were studied by petrography (immersion analysis of samples in transmitted light on a Polam-211 polarization microscope) and x-ray phase analysis (a STOE diffractometer, FR-552 monochromator chamber, reference standard — germanium, cathode — copper, radiation $K_{\alpha 1}$). The results of these analyses are listed in Table 2.

After the powder was separated from acid by filtration and rinsing with water on a filter, the filtrate was turbid, especially that of powders synthesized at 800°C. This shows that part of the nanoparticles of solid solutions of Al_2O_3 in $MgAl_2O_4$ has passed into the liquid and through the filter.

If only the amount of MgO in excess of stoichiometry were dissolved, the loss would be 12.4 wt.%. The initial oxide mixture had 37.3 wt.% MgO and 62.7 wt.% Al_2O_3. As can be seen from Table 1, the weight losses in all cases exceed 12.4 wt.% and for the composition without additives synthesized at 800°C the loss is equal to 37.3 wt.%. An increase in the temperature of synthesis to 1100°C sharply decreases the weight loss. Compositions synthesized from oxides with additives have significantly lower weight losses. The difference is especially perceptible in the compositions synthesized at 800°C. This agrees with the theory stated above.

It should be noted that the results of petrography and x-ray phase analysis for highly dispersed (especially nano-size) powders can differ significantly. Petrographic data essentially depend on the skill of the petrographer, especially in studying highly dispersed powders in which the particle size is at the boundary of the method sensitivity. Although x-ray phase analysis at the stage of recording of spectra is more objective, it should be noted that highly dispersed particles frequently have a highly distorted structure, up to an amorphous one. As a consequence, some peaks decrease, or even disappear in the case of an amorphous structure. In this case the content of a phase content can be judged based on the magnitude of the peaks only with great reservation. Based on the peak magnitude, a well-crystallized phase, even when its amount is significantly smaller, inevitably dominates over a poorly crystallized phase.

Petrographic analysis (Table 2) has established that powders synthesized at 800°C, both with and without additives, contain aluminomagnesian spinel as the main phase; its particle size in both cases is significantly smaller than 1 μm. No free magnesium and aluminum oxides have been detected. The refractive index of spinel is decreased (1.716), which can be attributed to magnesium oxide interlayers on the surface of spinel particles, which cannot be detected against the background of spinel, the particle sizes being so small. It has been impossible to find a difference between the powders with and without additives.

According to x-ray phase analysis data based on the magnitude and definiteness of the peaks, MgO is the main phase in the powders with and without additives (Table 2). The powder without additives contains half as much spinel and the powder with additives has three times less spinel than MgO.

Magnesium oxide has a simple cubic lattice and can quickly perfect it by means of diffusion mass transfer, which ensures the emergence of clear and high peaks. Spinel (or, more precisely, solid solution of Al_2O_3 in $MgAl_2O_4$) is poorly crystallized and part of its nanoparticles are amorphous. At the same time, the lower (according to x-ray phase analysis) content of spinel points to the fact that the additive delays the synthesis of solid solutions of Al_2O_3 in $MgAl_2O_4$.

After calcination at 1100°C, the results of petrographic and x-ray phase analysis of powders with and without additives differ significantly as well (Table 2).

According to petrography analysis, the main phase in the powder without additives is stoichiometric aluminomagnesian spinel (more perfect than the spinel produced at 800°C) with a refractive index of 1.716. The size of spinel particle ranges from 1 to 2 μm. Furthermore, crystals are present (not more than 3 wt.%) in which the refractive index varies across the crystal from a higher to a lower value (more than 1.716 in the center of the crystal and less than 1.716 near the grain boundary), i.e., a solid solution with a higher Al_2O_3 content prevails in the center of the crystal and a solution with a higher content of MgO prevails near the crystal boundaries. The size of solid solution particles is 0.5 – 0.8 μm. The for-

TABLE 2

Synthesized powder	Analysis method	Synthesis at temperature 800°C		Synthesis at temperature 1100°C	
		without additives	with additives	without additives	with additives
Without treatment	X-ray phase analysis	MgO, quantity of spinel half as much	MgO, quantity of spinel 3 times less	Spinel, quantity of MgO half as much, about 3 wt.% corundum	Spinel, slightly less MgO, about 3 wt.% corundum
Without treatment	Petrography	Spinel	Spinel	Spinel, solid solution of Al_2O_3 in spinel in the center of crystals	Stoichiometric spinel
HCl-treated: filtered powders: heat treatment at 600°C	X-ray phase analysis	Spinel, half as much corundum	Spinel, no corundum	Spinel, very little corundum	Spinel, very little corundum
drying	Petrography	Spinel, $MgCl_2 \cdot nH_2O$	Spinel, $MgCl_2 \cdot nH_2O$	Spinel, $MgCl_2 \cdot nH_2O$	Spinel, a little $MgCl_2 \cdot nH_2O$
filtrate: heat-treatment at 800°C	X-ray phase analysis	MgO, a little spinel	MgO, a little spinel, but better crystallized	MgO, traces of spinel	MgO, traces of spinel
heat treatment at 1500°C	X-ray phase analysis	MgO, about 30 wt.% spinel	MgO, about 15 wt.% spinel	MgO, about 7 wt.% spinel	MgO, about 3 wt.% spinel
drying	Petrography	Spinel	Spinel, $MgCl_2 \cdot nH_2O$	$MgCl_2 \cdot nH_2O$	$MgCl_2 \cdot nH_2O$

mation of excess MgO along the crystal boundaries agrees with the theory presented above.

According to petrography data, powder synthesized from oxides with additives is nearly monofractional, with the spinel particle size below 1 μm, and the main phase is aluminomagnesian spinel with a refractive index of 1.718. No solid solutions have been identified.

The data of x-ray phase analysis for samples with and without additives demonstrate that the main peaks belong to spinel and magnesium oxide. No perceptible shift in the peaks pointing to the formation of solid solutions has been registered. Based on the magnitude of the most intense peaks, the content of MgO in the powder without additives is approximately half as much as the content of spinel and in the powder with additives only slightly lower that the content of spinel. Furthermore, both samples have corundum peaks (based on the intensity of the mains peaks, its weight content is approximately 3%). The absence of corundum in the petrographic analysis and its presence in x-ray phase analysis presumably indicates that the solid solutions of Al_2O_3 in $MgAl_2O_4$ after heat treatment at 1100°C become very unstable and start disintegrating and forming Al_2O_3 nanoparticles which cannot yet be identified by a petrographer, but can already be registered by x-ray phase analysis.

Although, according to x-ray phase analysis, the composition without additives has less MgO, a larger quantity of MgO dissolves in acid (Table 1). It can be assumed that the compositions without additives have a larger quantity of nanoparticles of the solid solutions of Al_2O_3 in $MgAl_2O_4$, which pass into the acid solution and, accordingly, increase the weight loss.

Petrographic analysis of spinel powder synthesized at 800°C without additives and then treated with HCl and dried has established the presence of spinel crystals enriched in $MgCl_2$ along their peripheries (the same situation as in the filtrate). At the periphery of spinel crystals discontinuous interlayers are formed by $MgCl_2 \cdot nH_2O$.

X-ray phase analysis of spinel powder synthesized at 800°C without additives, treated with HCl, and calcined at 600°C indicates that the main phases are spinel and corundum (the amount of corundum is half as much, judging by its peaks, but this result is obviously exaggerated due to the perfect corundum structure). This may be a consequence of the disintegration of unstable supersaturated solid spinel solutions (Al_2O_3 in $MgAl_2O_4$) after their repeated heat treatment at the temperature of 600°C.

Petrographic analysis of spinel powder synthesized at 800°C with additives, treated with HCl, and dried also corroborates the presence of spinel crystals, which are enriched in $MgCl_2$ along their periphery (the same picture as in the case of the powder without additives). At the periphery of spinel crystals discontinuous interlayers are formed by $MgCl_2 \cdot nH_2O$ as well.

X-ray phase analysis of spinel powder treated with HCl and calcined at 600°C has identified spinel as the main phase, but corundum is absent. Solid spinel solutions synthesized from oxides with additives are more steady and do not disintegrate under additional heat treatment at 600°C.

Petrographic analysis of spinel powder synthesized at 1100°C without additives, HCl-treated, and dried has confirmed that $MgCl_2 \cdot nH_2O$ is present in significantly smaller quantities than in the similar powder synthesized at 800°C.

X-ray phase analysis of spinel powder synthesized at 1100°C without additives treated with HCl, and calcined at 600°C shows that the main phase is spinel and there is very little corundum (even judging from the peaks, its quantity is

15 times lower). The dissolved particles are mainly excess MgO and nanoparticles of the solid spinel solution.

Petrographic analysis of spinel powder synthesized at 1100°C with additives, HCl-treated, and dried also gives a very similar picture, but $MgCl_2 \cdot nH_2O$ is present is smaller quantities than in the powder synthesized without additives. This agrees with the weight loss data (Table 1).

According to x-ray phase analysis, spinel powder synthesized at 1100°C with additives, HCl-treated, and calcined at 600°C contains spinel as the main phase and traces of corundum. This powder in fact does not differ from the powder without additives, which agrees with the solubility data. The dissolved particles are mainly excess MgO and very few nanoparticles of the solid spinel solution.

Petrographic analysis of dried filtrates formed after the separation of rinsed HCl powders on a filter shows the following. The dried filtrate resulting from rinsing the powder of spinel synthesized at 800°C without additives contains aggregates up to 6 μm consisting of spinel crystals which are enriched with $MgCl_2$ along their periphery. Free $MgCl_2$ has not been detected.

X-ray phase analysis of the filtrate resulting from rinsing spinel powder synthesized at 800°C without additives and calcined at 600°C shows that the main phase is MgO with a small quantity of spinel.

X-ray analysis after calcinating the filtrate at 1500°C shows that its main phases are MgO and a large (approximately 30 wt.%) amount of spinel (more than in all other filtrate samples treated at 1500°C and twice as much as in the filtrate after dissolving the powder with additives). The petrographic and x-ray diffraction data confirm that spinel nanoparticles pass into the solution.

The dried filtrate after rinsing spinel powder synthesized at 800°C with additives also contains aggregates of size up to 6 μm consisting of spinel crystals which are enriched with $MgCl_2$ along their periphery. At the same time, we register the presence of free $MgCl_2 \cdot nH_2O$ that is not bound to the spinel.

X-ray phase analysis of the filtrate resulting from drying spinel powder synthesized at 800°C with additives and calcined at 600°C yielded essentially the same results as the filtrate without additives. The main phase is MgO and a small quantity of spinel, but its peaks are better defined (spinel is better crystallized) than in the composition without additives. The x-ray phase analysis of the same powder after additional calcination at 1500°C indicates that the main phase is MgO and the amount of spinel is half as much as in the composition without additives (about 15 wt.%). Apparently, after rinsing spinel powder synthesized at 800°C (with and without additives) spinel nanoparticles pass via the filter into the filtrate, which accounts for the high solubility of the powder and the presence of spinel in calcined filtrate.

According to petrographic analysis, the dried filtrate after rinsing spinel powder synthesized at 1100°C without additives does not contain spinel and contains only crystals of

$MgCl_2 \cdot nH_2O$, their shape ranging from plates of size below 1 μm to prismatic crystals of size up to 2 μm.

X-ray phase analysis of the filtrate resulting from rinsing spinel powder synthesized at 1100°C without additives and calcined at 600°C yielded results consistent with the petrographic analysis. The main phase is MgO and traces of spinel (spinel particles are poorly crystallized). X-ray phase analysis after additional calcination at 1500°C demonstrated that the main phase is MgO and a small quantity of spinel (about 7 wt.%).

The dried filtrate after rinsing spinel powder synthesized at 1100°C with additives does not contain spinel either, and only contains $MgCl_2 \cdot nH_2O$ crystals of size below 1 μm.

According to x-ray phase analysis, the filtrate resulting from rinsing spinel powder synthesized at 1100°C without additives and calcined at 600°C contains MgO as the main phase and traces of spinel. There are fewer spinel peaks (only two, although intense) than in the composition without additives. X-ray phase analysis of this powder after additional calcination at 1500°C indicates that the main phase is MgO and a small quantity of spinel (about 3 wt.%). This shows that upon rinsing spinel powder synthesized at 1100°C from a mixture of oxides with additives, it is mainly free MgO that becomes dissolved.

A comparison of petrographic and x-ray diffraction analysis data (Table 2) with weight losses after HCl treatment (Table 1) suggests that the dissolving materials are free MgO not fixed in the solid solutions of Al_2O_3 in $MgAl_2O_4$ and the nanoparticles of these solid solutions. The temperature of synthesis of $MgAl_2O_4$ with a 10% MgO excess and the presence of additives affect the composition, particle size, quantity, and the degree of perfection of the crystalline structure of solid solutions of Al_2O_3 in $MgAl_2O_4$. Increasing the temperature decreases the content of Al_2O_3 in $MgAl_2O_4$ due to the dissolution of MgO in it, and the composition approaches that of the stoichiometric spinel. The introduction of additives into the initial oxides produces a similar effect. However, under a low temperature of synthesis (800°C) the additives delay synthesis. This decreases the amount of the solid spinel solutions formed (Table 2), but they have larger particle sizes and do not pass into solution, which sharply decreases the weight losses (Table 1).

The experiments performed indicate that delaying the diffusion rate of magnesium cations and increasing the diffusion rate of aluminum cations in the synthesis of $MgAl_2O_4$ with 10% MgO from a mixture of highly disperse simple oxides has a substantial effect on the solubility of the products of synthesis in hydrochloric acid. The use of additives and an increased temperature of synthesis decrease the solubility of powders in hydrochloric acid.

In our study the diffusion rate of magnesium cations was decreased by introducing a Na_2O additive causing the formation of oxygen vacancies: reaction (1). The diffusion rate of aluminum cations in Al_2O_3 was raised by introducing a TiO_2

additive causing the formation of aluminum vacancies, i.e., reaction (2).

In the synthesis of spinel from highly disperse powders, initially solid solutions of Al_2O_3 in $MgAl_2O_4$ are formed, whereas MgO that remains not fixed to the spinel becomes dissolved in HCl. The dissolution of powders synthesized at 800°C facilitates transition into solution of nanoparticles of solid solutions of Al_2O_3 in $MgAl_2O_4$. These nanoparticles in the form of a sol penetrate through the filter and make the filtrate opalescent. This leads to intense dissolution of the synthesized powder, significantly exceeding not only its content of excess MgO (12.4 wt.%) compared to the stoichiometric composition, but even its total content in the synthesized mixture (37.3 wt.%). However, in this case also the dissolution can be reduced by more than half in the case of using additives (Table 1). This can be explained by the fact that a larger quantity of MgO in the presence of additives becomes fixed in the solid solutions of Al_2O_3 in $MgAl_2O_4$ (accordingly, the solid solutions contain less Al_2O_3).

Experimental data confirm the assumption that in the synthesis of spinel from highly dispersed oxide, initially solid solutions of Al_2O_3 in $MgAl_2O_4$ are formed, which gradually becomes saturated with MgO, bringing the composition closer to a stoichiometric spinel. Even an excess of MgO (10%) does not prevent the initial formation of solid solutions of Al_2O_3 in $MgAl_2O_4$. The use of additives and an increase in temperature contribute to the solid solutions of Al_2O_3 in $MgAl_2O_4$ approaching the stoichiometric spinel composition.

There are many natural nonstoichiometric compounds whose range of existence is nearly one-sided. When such compounds are synthesized from a mixture of highly dispersed oxides, at first we observe the formation of a solid solution of the oxide with the lower diffusion rate in the synthesized compound. As a result, part of the oxide with the higher diffusion mass transfer rate may persist in the free state; accordingly, the compound has a nonstoichiometric composition. Modification of the mass transfer rates of the cations comprising the complex oxide is promising for obtaining a stoichiometric composition from highly disperse oxides whose cation diffusion rates differ significantly.

The mass transfer rates in initial highly dispersed oxides can be modified by introducing additives that form solid solutions. When substitutional solid solutions are synthesized in an initial simple oxide (according to Schottky), the formation of oxygen vacancies decreases the cation mass transfer rate, whereas the formation of cation vacancies increases this rate. This opens possibilities for accelerating the synthesis of complex oxides of a composition approaching the stoichiometric one, which will make it possible to lower the temperature of synthesis of complex oxides with a nearly stoichiometric composition and decrease the size of resulting powder particles.

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